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(54) Title: HYDROPHOBIC ORGANOSILICATE–MODIFIED SILICA GELS

(57) Abstract

The present invention is hydrophobic organosilicate–modified silica gels and a method for their preparation. The method comprises two steps, where in the first step an organosilicate–modified silica hydrosol is heat treated in the presence of a strong mineral acid at a pH less than pH 1 to form an organosilicate–modified silica hydrogel. In the second step, the organosilicate–modified silica hydrogel is contacted with an organosilicon compound in the presence of a catalytic amount of a strong acid to effect hydrophobing of the organosilicate–modified silica hydrogel thereby forming a hydrophobic organosilicate–modified silica hydrogel having a surface area within a range of 100 m^2/g to 750 m^2/g as measured in the dry state. In a preferred method, the hydrophobic organosilicate–modified silica gel is contacted with a sufficient quantity of a water–immiscible organic solvent to convert the hydrophobic organosilicate–modified silica hydrogel into a hydrophobic organosilicate–modified silica organogel.

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HYDROPHOBIC ORGANOSILICATE-MODIFIED SILICA GELS

The present invention is hydrophobic organosilicate-modified silica gels and method for their preparation. The method comprises two-steps, where in the first step an organosilicate-modified silica hydrosol is heat treated in the presence of a strong mineral acid at a pH less than pH 1 to form an organosilicate-modified silica hydrogel. In the second step the organosilicate-modified silica hydrogel is contacted with an organosilicon compound in the presence of a catalytic amount of a strong acid to effect hydrophobing of the organosilicate-modified silica hydrogel thereby forming a hydrophobic organosilicate-modified silica hydrogel having a surface area within a range of 100 m^2/g to 750 m^2/g as measured in the dry state. In a preferred method the hydrophobic organosilicate-modified silica hydrogel is contacted with a sufficient quantity of a water-immiscible organic solvent to convert the hydrophobic organosilicate-modified silica hydrogel into a hydrophobic organosilicate-modified silica organogel. The organic solvent can then be removed from the organogel to form a dry hydrophobic organosilicate-modified silica gel having a surface area within a range of 100 m^2/g to 750 m^2/g as measured in the dry state. A water soluble compound of cerium or iron may be added in the second step to improve the heat stability of the hydrophobic organosilicate-modified silica gel.

Although hydrophobic organosilicate-modified silica gels prepared by the present method are useful in many applications such as reinforcing and extending filler in organic rubbers, thermal insulation, and as filler in floatation devices, they are particularly useful as reinforcing fillers in silicone rubber compositions. It is well known that silicone rubbers formed from the vulcanization of polydiorganosiloxane fluids or gums alone generally have low elongation and tensile strength values. One means for improving the physical properties of such silicone rubbers involves the incorporation of a reinforcing silica filler into the fluid or gum prior to curing. However, silica reinforcing fillers have a tendency to interact with the polydiorganosiloxane fluid or gum causing a phenomenon typically referred to as "crepe hardening." A great deal of effort has been made in the past to treat the surface of reinforcing silica fillers with organosilanes or organosiloxanes to make the surface of the silica hydrophobic. This surface treatment reduces or diminishes the tendency of the compositions to crepe harden and improves the physical properties of the cured silicone rubber.

The prior art is represented by U.S. Patent No. 3,024,126; U.S. Patent No. 3,979,546; U.S. Patent No. 3,015,645; U.S. Patent No. 3,122,520; U.S. Patent No. 2,892,797; U.S. Patent No. 3,850,971; U.S. Patent No. 4,006,175 and U.S. Patent No. 4,360,388.

The hydrophobic organosilicate-modified silica gels prepared by the present method have improved hydrophobicity when compared to hydrophobic silica gels prepared without the presence of the organosilicate. The improved hydrophobicity can make the hydrophobic organosilicate-modified silica gels more compatible with organic rubber and silicone rubber compositions. The hydrophobic organosilicate-modified silica gels also have a lower refractive index, which makes them desirable for use in silicone rubber compositions requiring optical clarity.

The method for preparing the hydrophobic organosilicate-modified silica gels comprises:

(A) heating an organosilicate-modified silica hydrosol comprising (i) 2 to 50 weight percent of SiO_2 per milliliter and (ii) 1 to 50 weight percent of an organosilicate described by formula $R^1SiO_{3/2}$, where R^1 is a monovalent hydrocarbon radical comprising 1 to 6 carbon atoms, in the presence of a strong mineral acid at a pH less than pH 1 and a temperature within a range of 20 to 250°C. to form an organosilicate-modified silica hydrogel, and

(B) contacting the organosilicate-modified silica hydrogel with (1) a catalytic amount of a strong acid and (2) an organosilicon compound selected from organosilanes described by formula $R^2_aH_bSiX_{4-a-b}$ (1) and organosiloxanes described by formula $R^2_nSiO_{(4-n)/2}$ (2) where each R^2 is independently selected from hydrocarbon radicals comprising 1 to 12 carbon atoms and organofunctional hydrocarbon radicals comprising 1 to 12 carbon atoms, each X is independently selected from halogen and alkoxy radicals comprising 1 to 12 carbon atoms, a=0, 1, 2, or 3, b=0 or 1, a+b=1, 2, or 3 with the proviso that when b=1 then a+b=2 or 3, and n is an integer of from 2 to 3 inclusive to form a hydrophobic organosilicate-modified hydrogel having a surface area within a range of 100 m^2/g to 750 m^2/g as measured in the dry state.

Hydrophobic organosilicate-modified silica gels prepared by the present method are useful as reinforcing fillers in silicone rubber and organic rubber compositions.

The method used to prepare the organosilicate-modified silica hydrosol is not critical and can be any of those known in the art. The organosilicate modified silica hydrosol may be prepared by first preparing a silica hydrosol and then mixing the silica hydrosol with an organosilicate as described herein and acidifying the mixture. The organosilicate-modified silica hydrosol may be prepared by mixing a silica hydrosol with an acidified organosilicate. The organosilicate-modified silica hydrosol may be prepared by forming a mixture of sodium silicate and the organosilicate and acidying the mixture. Silica hydrosols useful for preparing the organosilicate-modified silica hydrosol can be prepared by deionizing sodium silicate by a method such as the use of an ion exchange resin. The silica hydrosol may be prepared by hydrolyzing a silane at a low temperature. The silica hydrosol may be prepared by acidifying a sodium silicate mixture.

Organosilicates useful in the present method are described by formula $R^1SiO_{3/2}$, where R^1 is a monovalent hydrocarbon radical comprising 1 to 6 carbon atoms. R^1 can be alkyls such as methyl, ethyl, and hexyl; substituted alkyls such as 3,3,3-trifluoropropyl and chloromethyl; alkenyls such as vinyl, allyl and hexenyl; and aryls such as phenyl.

The organosilicate-modified silica hydrosol requires the presence of 2 to 50 weight percent of SiO_2 per milliliter (ml) of the hydrosol. Preferred is when the organosilicate-modified silica hydrosol comprises 5 to 20 weight percent of SiO_2 per ml of the hydrosol. The organosilicate-modified silica hydrosol also requires the presence of 1 to 50 weight percent of an organosilicate described by formula $R^1SiO_{3/2}$, where R^1 is described above, per ml of the hydrosol. Preferred is when the organosilicate-modified silica hydrosol comprises 10 to 35 weight percent of the organosilicate per ml of the hydrosol.

In step (A), the organosilicate-modified silica hydrosol must comprise a sufficient concentration of a strong mineral acid such that the pH of the organosilicate-modified silica hydrosol is less than pH 1. Preferably, there should be a sufficient amount of the strong mineral acid present so that the pH is essentially 0, that is so that the pH cannot be measured. For the purpose of this invention any strong mineral acid can be used. As used herein, the term "strong mineral acid" refers to those acids which ionize to the extent of at least 25 percent in 0.1 N aqueous solution at 18°C. The strong mineral acid may be hydrochloric, hydroiodic, sulfuric, nitric and phosphoric acid.

In step (A), the organosilicate-modified silica hydrosol must be heated at a temperature within a range of 20 to 250°C. Preferred is when the organosilicate-modified silica hydrosol is heated at a temperature within a range of 75 to 150°C. Even more preferred is when, in step (A), the organosilicate-modified silica hydrosol is heated at a temperature within a range of 90 to 110°C.

In step (A), the length of the heating time required varies with the temperature and acid concentration. Generally the higher the temperature and the greater the acid concentration the shorter the length of the heating time needed. The heating of step (A) must be continued until the organosilicate-modified silica hydrogel acquires a structure such that the final product after hydrophobing has a surface area in the dry state within a range of 100 m^2/g to 750 m^2/g as determined by the Brunauer Emmett and Teller (BET) method described in the Jour. Am. Chem. Soc. 60:309 (1938) and as further described in U.S. Patent No. 3,122,520. The surface area of the organosilicate-modified silica hydrogel at the conclusion of step (A) is immaterial provided it is such that the surface area of the dried product after the hydrophobing of step (B) is within the above described range. Generally the surface area of the organosilicate-modified silica hydrogel is reduced by the hydrophobing reaction, since the organosilyl groups which become attached to the surface of the organosilicate-modified silica hydrogel increase the average particle size. The surface of the organosilicate-modified silica hydrogel can be above 750 m^2/g provided that the hydrophobing treatment brings it within a range of 100 m^2/g to 750 m^2/g. To determine the proper heating conditions during conduct of step (A) it is necessary to proceed with the hydrophobing of step (B) and then measure the surface area of the resulting product in the dry state. If the surface area of the resulting product in the dry state is above 750 m^2/g, then the acid heating conditions of step (A) were too mild. If the surface area of the resulting product in the dry state is below 100 m^2/g, then the acid heating conditions of step (A) were too severe. Examples of suitable acid concentrations, temperatures and lengths of time for conduct of step (A) are provided in the examples herein. If the surface area of the hydrophobic organosilicate-modified silica gel in the dry state is above or below the described range, the hydrophobic organosilicate-modified silica gels have diminished reinforcing properties in silicone elastomers.

If desired, the organosilicate-modified silica hydrogel of step (A) may be subjected to a shearing force to reduce aggregate particle size and to improve the uniformity

of the particle size distribution prior to the conduct of the hydrophobing reaction of step (B). The shearing may be applied to the organosilicate-modified silica hydrogel by any of those methods known in the art. The shearing force may be applied by a mechanical means such as a high-speed mixer or by ultrasound. This reduction in aggregate particle size and improved uniformity of particle size can provide for hydrophobic organosilicate-modified silica gels which when compounded into silicone elastomer compositions provide for lower viscosity compositions, more stable compositions, and for cured silicone elastomers having improved clarity and physical properties.

In step (B) of the present method the organosilicate-modified silica hydrogel of step (A) is mixed with one or more of the defined organosilicon compounds described by formulas (1) and (2) in the presence of a catalytic amount of a strong acid. In step (B), the strong acid can be the same acid which was used in step (A). However, if desired the organosilicate-modified silica hydrogel can be washed free of acid and a catalytic amount of strong acid added either prior to, simultaneously with, or subsequent to the addition of the organosilicon compound. In the case where the organosilicon compound is a chlorosilane, the catalytic amount of the strong acid can be generated in situ by hydrolysis of the chlorosilane or the reaction of the chlorosilane directly with hydroxyls of the organosilicate-modified silica hydrogel. In step (B) the limitations on pH as described for step (A) do not apply. It is only necessary that a catalytic amount of a strong acid be present in an amount sufficient to effect reaction of the organosilicon compound with the organosilicate-modified silica hydrogel. Examples of useful acids include hydrochloric, sulfuric, and benzene sulfonic acids. It is preferred that in step (B) the strong acid catalyst provide a pH less than 2.5.

The temperature at which the hydrophobing of step (B) is conducted is not critical and can be from 20 to 250°C. Generally, it is preferred that the hydrophobing of step (B) be conducted at a temperature within a range of 30 to 150°C. The hydrophobing of step (B) can be conducted at the reflux temperature of the water-immiscible organic solvent when it is present.

In step (B), the organosilicate-modified silica hydrogel of step (A) is reacted with an organosilicon compound described by formula (1) or (2). In formulas (1) and (2), each R^2 can be independently selected from hydrocarbon radicals comprising 1 to 12 carbon atoms and organofunctional hydrocarbon radicals comprising 1 to 12 carbon atoms.

R^2 can be a saturated or unsaturated hydrocarbon radical. R^2 can be a substituted or non-substituted hydrocarbon radical. R^2 can be alkyl radicals such as methyl, ethyl, t-butyl, hexyl, heptyl, octyl, decyl, and dodecyl; alkenyl radicals such as vinyl, allyl, and hexenyl; substituted alkyl radicals such as chloromethyl, 3,3,3-trifluoropropyl and 6-chlorohexyl; and aryl radicals such as phenyl, naphthyl and tolyl. R^2 can be an organofunctional hydrocarbon radical comprising 1 to 12 carbon atoms where the functionality is mercapto, disulfide, polysulfide, amino, carboxylic acid, carbinol, ester, or amido. Preferred organofunctional hydrocarbon radicals are those having mercapto or tetrasulfide functionality.

In formula (1) each X is independently selected from halogen and alkoxy radicals comprising 1 to 12 carbon atoms. When X is a halogen, it is preferred that the halogen be chlorine. When X is an alkoxy radical, X may be methoxy, ethoxy and propoxy. Preferred is where each X is selected from chlorine atoms and methoxy.

The viscosity of the organosiloxanes described by formula (2) is not limiting and can range from that of a fluid to a gum. Generally, higher molecular weight organosiloxanes will be cleaved by the acidic conditions of the present method allowing them to react with the organosilicate-modified silica hydrogel.

The organosilicon compound may be provided to the present method as a single compound as described by formula (1) or (2) or as a mixture of two or more organosilicon compounds described by formulas (1) and (2).

Examples of useful organosilicon compounds include diethyldichlorosilane, allylmethyldichlorosilane, methylphenyldichlorosilane, phenylethyldiethoxysilane, 3,3,3-trifluoropropylmethyldichlorosilane, trimethylbutoxysilane, sym-diphenyltetramethyldisiloxane, trivinyltrimethylcyclotrisiloxane, hexaethyldisiloxane, pentylmethyldichlorosilane, divinyldipropoxysilane, vinyldimethylchlorosilane, vinyldimethylmethoxysilane, vinylmethyldichlorosilane, trimethylchlorosilane, hexamethyldisiloxane, hexenylmethyldichlorosilane, dimethylchlorosilane, dimethyldichorosilane, mercaptopropylmethyldimethoxysilane and bis{3-(triethoxysilyl)propyl}tetrasulfide. When the hydrophobic organosilicate-modified silica gel is to be used as a filler in silicone rubber, it is preferred that the organosilicon compound be hexamethyldisiloxane or dimethyldichlorosilane.

The amount of organosilicon compound added to the method is that

sufficient to adequately hydrophobe the organosilicate-modified silica hydrogel to provide a hydrophobic organosilicate-modified silica gel suitable for its intended use. Generally, the organosilicon compound should be added to the method in an amount such that there is at least 0.04 organosilyl unit per SiO_2 unit in the organosilicate-modified silica hydrogel. The upper limit of the amount of organosilicon compound added to the process is not critical since any amount in excess of the amount required to saturate the organosilicate-modified silica hydrogel will act as a solvent for the method.

The hydrophobic organosilicate-modified silica hydrogel of step (B) may be used as is or may be recovered for use by such methods as centrifugation or filtration. The hydrophobic organosilicate-modified silica hydrogel may be dried by the use of such methods as heating or reducing pressure or a combination of both heating and reducing pressure.

In a preferred method, a water-immiscible organic solvent in sufficient amount to convert the organosilicate-modified silica hydrogel or hydrophobic organosilicate-modified silica hydrogel to the corresponding organogel is added. The organic solvent can be added prior to, simultaneously with, or subsequent to the addition of the organosilicon compound. That is, the organosilicate-modified silica hydrogel can be first converted into an organogel by replacement of the water with the organic solvent and then hydrophobed. On the other hand, the organosilicon compound and the organic solvent can be added simultaneously to the organosilicate-modified silica hydrogel. Under these conditions, the reaction of the organosilicate-modified silica hydrogel with the organosilicon compound and the replacement of the water in the hydrophobed organosilicate-modified silica hydrogel with the organic solvent may occur simultaneously. Finally, the organosilicon compound can be added prior to the organic solvent, in which case the organosilicate-modified silica hydrogel reacts with the organosilicon compound and the resulting product is then converted into an organogel by an addition of an organic solvent. In the latter two cases, the conversion to the organogel is accomplished by a phase separation, in which the hydrophobed organosilicate-modified silica hydrogel passes into the organic solvent phase. A preferred method is where a water-immiscible organic solvent is added after formation of the hydrophobic organosilicate-modified silica hydrogel thereby effecting formation of the corresponding organogel.

For purposes of this invention, any organic solvent immiscible with water can be employed. Suitable water-immiscible organic solvents include low molecular

weight siloxanes such as hexamethyldisiloxane, octamethylcyclotetrasiloxane, diphenyltetramethyldisiloxane and trimethylsilyl endblocked dimethylpolysiloxane fluids. When a siloxane is employed as a solvent it may serve both as a solvent and as a reactant with the organosilicate-modified silica hydrogel. In addition, suitable solvents include hydrocarbons such as toluene, xylene, heptane and other aliphatic hydrocarbon solvents and cyclohexane, ethers such as diethylether and dibutylether, halohydrocarbon solvents such as methylene chloride, chloroform, ethylene chloride and chlorobenzene, and ketones such as methylisobutylketone.

The amount of solvent is not critical so long as there is sufficient solvent to convert the organosilicate-modified silica hydrogel or hydrophobic organosilicate-modified silica hydrogel into the corresponding organogel. Preferably, the solvent should have a boiling point below 250°C. to facilitate its removal from the hydrophobic organosilicate-modified silica organogel, however, the boiling point is not critical since the solvent may be removed from the hydrophobic organosilicate-modified silica organogel by centrifuging or other suitable means.

The hydrophobic organosilicate-modified silica organogel may be used directly as a reinforcing agent in silicone rubber or in any other uses for which this type of product can be used. Alternatively, the water-immiscible organic solvent may be removed from the hydrophobic organosilicate-modified silica organogel and the resulting dry hydrophobed organosilicate-modified silica gel used.

During the conduct of step (B) it may be desirable to add a surfactant or water-miscible solvent to facilitate the reaction of the organosilicon compound with the organosilicate-modified silica hydrogel. The surfactant or water-miscible solvent may be added in the presence or absence of any water-immiscible organic solvent added to the method. Suitable surfactants can include anionic surfactants such as dodecylbenzene sulfonic acid, nonionic surfactants such as polyoxyethylene(23)lauryl ether and $(Me_3O)_2MeSi(CH_2)_3(OCH_2CH_2)_7OMe$ where Me is methyl, and cationic surfactants such as N-alkyltrimethyl ammonium chloride. Suitable water miscible solvents can include alcohols such as ethanol, propanol, isopropanol, n-butanol and tetrahydrofuran.

In step (B) of the present method, an effective amount of a heat stabilizing agent selected from a group consisting of water soluble compounds of cerium and iron may be added. By the term "effective amount", it is meant that the water soluble compound of cerium or iron is present in the hydrophobic organosilicate-modified silica gel at a

concentration sufficient to provide improved heat stability to those compositions in which the hydrophobic organosilicate-modified silica gel is incorporated. Such compositions can include silicone rubber, natural rubber and synthetic organic rubber.

Generally, 0.01 percent weight/volume (% Wt./Vol.) to 10 %Wt./Vol. of the water soluble compound of cerium or iron in relation to the volume of components in step (B), excluding solvents, is considered useful in the present process. Preferred is where the water soluble compound of cerium or iron comprises 0.1 %Wt./Vol. to 1 %Wt./Vol. on the same basis.

Examples of water soluble compounds which may be useful in the present method include $FeCl_3$, $FeBr_2$, $FeBr_3.6H_2O$, $FeCl_2.4H_2O$, $FeI_2.4H_2O$, $Fe(NO_3)_3.6H_2O$, $FePO_4.2H_2O$, $CeCl_3.9H_2O$, $CeBr_3.H_2O$, $CeI_3.9H_2O$, $Ce(NO_3)_3.6H_2O$, and $Ce(SO_4)_2.2H_2O$. A preferred water soluble compound of cerium or iron for use in the present method is selected from $FeCl_3$ and $CeCl_3.9H_2O$.

The following examples are provided to illustrate the present invention. These examples are not intended to limit the scope of the present claims.

Example 1

A phenylsilicate-modified silica gel hydrophobed with hexamethyldisiloxane and heat stabilized with $FeCl_3$ was prepared. A phenylsilicate having the average formula $Na_2O(PhSiO_{1.5})_{0.67}$, where Ph represents phenyl, was prepared as follows. Into a flask equipped with stirrer, addition funnel and distillation head with a condenser was placed 309 g of a 48.4% NaOH solution and 130 ml of deionized water. To this solution was added 250 g of $PhSi(OMe)_3$ over a period of 30 minutes, with an exotherm causing the temperature to increase to 49°C. The content of the flask was heated to 70°C. for 45 minutes and then stripped free of methanol by distillation. The product remaining in the flask was clear in color and weighed 543 g.

A silicate mixture was formed comprising 482.2 ml of PQ N Clear Sodium Silicate (PQ Corporation, Valley Forge, PA) diluted with 752 ml of deionized water and 111 ml of $Na_2O(PhSiO_{1.5})_{0.67}$ diluted with 752 ml of deionized water. This silicate mixture was allowed to stand overnight. The silicate mixture was added, with stirring, to a solution comprising 260 ml of concentrated HCl (Fisher Certified, Fisher Scientific, Fair Lawn, NJ) diluted with 640 ml of deionized water. The resulting phenylsilicate-modified

silica hydrosol was adjusted to pH 2.5.

The phenylsilicate-modified silica hydrosol was deionized by pumping through a 1.5 m x 5 cm column packed with 1.5 L of Dowex 50WX8-100 ion exchange resin in the acid form (The Dow Chemical Company, Midland, MI) at a rate of 60 ml per minute. The pH of the column effluent was monitored until the pH dropped below 0.5, at which point the next 3 L of deionized phenylsilicate-modified silica hydrosol effluent was collected.

The deionized phenylsilicate-modified silica hydrosol was agglomerated by placing 2 L of the deionized silica hydrosol in a 5 L flask and, while stirring, adding 626 ml of concentrated HCl (Fisher Certified). The phenylsilicate-modified silica hydrogel which formed within a few minutes of addition of the HCl was broken-up by additional stirring to form a phenylsilicate-modified silica hydrogel suspension. The phenylsilicate-modified silica hydrogel suspension was heat treated at 100°C. for 3 hours and then cooled to 40°C.

The phenylsilicate-modified silica hydrogel was hydrophobed as follows. To the phenylsilicate-modified silica hydrogel, with stirring, was added 872 ml of isopropanol followed by 2.6 g of ferric chloride ($FeCl_3$) and 112 ml of hexamethyldisiloxane. The resulting mixture was stirred for 45 minutes at room temperature. Then, 2.4 L of toluene were added to the mixture. This mixture was stirred for an additional 5 minutes, stirring stopped and the aqueous phase drained from the bottom of the flask. The toluene phase was washed with 1 L of deionized water. The flask was then fitted with a Dean-Stark trap and the toluene phase refluxed to remove residual water. The toluene phase was transferred to an open container in an exhaust hood and the toluene allowed to evaporate leaving as product a hydrophobic phenylsilicate-modified silica gel. The hydrophobic phenylsilicate-modified silica gel was dried overnight at 150°C. to remove residual toluene. The yield of hydrophobic phenylsilicate-modified silica gel was 162 g.

Example 2

A phenylsilicate-modified silica gel hydrophobed with hexenylmethyldichlorosilane and heat stabilized with $FeCl_3$ was prepared. A silicate mixture was formed comprising 482 ml of PQ N Clear Sodium Silicate (PQ Corporation) diluted with 752 ml of deionized water and 111 ml of $Na_2O(PhSiO_{1.5})_{0.67}$, prepared as described in Example 1, diluted with 752 ml of deionized water. The silicate mixture was

allowed to stand overnight before use. The silicate mixture was added, with stirring, to a solution comprising 260 ml of concentrated HCl (Fisher Certified) diluted with 640 ml of deionized water. The resulting phenylsilicate-modified silica hydrosol was adjusted to pH 2.5.

The phenylsilicate-modified silica hydrosol was deionized by the method described in Example 1. The phenylsilicate-modified silica hydrosol was agglomerated by placing 1 L of the silica hydrosol in a 5 L flask and, while stirring, adding 313 ml of concentrated HCl (Fisher Certified). The phenylsilicate-modified silica hydrogel which formed within a few minutes of addition of the HCl was broken-up by additional stirring to form a phenylsilicate-modified silica hydrogel suspension. The phenylsilicate-modified silica hydrogel suspension was heat treated at 100°C. for 3 hours and then cooled to 40°C.

The phenylsilicate-modified silica hydrogel was hydrophobed as follows. To the phenylsilicate-modified silica hydrogel, with stirring, was added 436 ml of isopropanol followed by 0.9 g of $FeCl_3$ and 34 ml of hexenylmethyldichlorosilane. The mixture was stirred for 45 minutes at room temperature. Then, 2.4 L of toluene were added to the mixture. This mixture was stirred for an additional 5 minutes, stirring stopped, and the aqueous phase drained from the bottom of the flask. The toluene phase was washed with 1 L of deionized water. The flask was then fitted with a Dean-Stark trap and the toluene phase refluxed to remove residual water. The toluene phase was transferred to an open container in an exhaust hood and the toluene allowed to evaporate leaving as product a hydrophobic phenylsilicate-modified silica gel. The hydrophobic phenylsilicate-modified silica gel was dried overnight at 150°C. to remove residual toluene. The yield of hydrophobic phenylsilicate-modified silica gel was 98 g.

Example 3

A methylsilicate-modified silica gel hydrophobed with hexamethyldisiloxane and heat stabilized by the addition of $FeCl_3$ was prepared. A solution was prepared comprising 256 ml of PQ N Clear Sodium Silicate (PQ Corporation), 213 ml of sodium methyl silicate (DC7722, Dow Corning Corporation, Midland, MI), and 847 ml of deionized water. This solution was transferred to a 5 L flask and 500 ml of concentrated HCL (Fisher Certified) were added to the flask. The content of the flask was refluxed for 3 hours forming a methylsilicate-modified silica hydrogel and then cooled to room

temperature.

To the methylsilicate-modified silica hydrogel, with stirring, was added 833 ml of isopropanol, 120 ml of hexamethyldisiloxane, and 4.2 g of $FeCl_3$. After stirring the flask content for 1 hour, 1.4 L of toluene were added to the flask. After stirring the flask content briefly, stirring was stopped and the aqueous phase drained from the flask. 250 ml of isopropanol and 60 ml of deionized water were added to the flask and the content of the flask stirred briefly Then, 690 ml of deionized water were added to the flask and after stirring briefly the aqueous phase was drained from the flask.

The flask was fitted with a Dean-Stark trap and the toluene phase refluxed to remove residual water. The toluene phase was poured into glass pans and the toluene evaporated leaving as product a hydrophobic methylsilicate-modified silica gel. The hydrophobic methylsilicate-modified silica gel was dried for 24 hours at 75°C. The yield of dried hydrophobic methylsilicate-modified silica gel was 158 g.

Example 4

An organosilicate-modified silica gel hydrophobed with hexamethyldisiloxane was prepared. A silica hydrosol was prepared comprising 283 ml of PQ N Clear Sodium Silicate (PQ Corporation), 65 ml of sodium methyl silicate (DC 722), 74 ml of a sodium phenylsilicate prepared as described in Example 1 and 978 ml of deionized water. The silica hydrosol was transferred to a 5 L flask and 500 ml of concentrated HCl (Fisher Certified) were added to the flask. The content of the flask was refluxed for 3 hours forming an organosilicate-modified silica hydrogel and then cooled to room temperature.

To the organosilicate-modified silica hydrogel, with stirring, was added 833 ml of isopropanol and 120 ml of hexamethyldisiloxane. After stirring the flask content for 1 hour, 2 L of toluene were added to the flask. After stirring the flask content briefly, stirring was stopped and the aqueous phase drained from the flask. Then 1 L of deionized water was added to the flask and, after brief stirring of the flask content, the aqueous phase was drained from the flask.

The flask was fitted with a Dean-Stark trap and the toluene phase refluxed to remove residual water. The toluene phase was poured into glass pans and the toluene evaporated leaving as product a hydrophobic organosilicate-modified silica gel. The hydrophobic organosilicate-modified silica gel was dried for 24 hours at 75°C. The

yield of dried hydrophobic organosilicate-modified silica gel was 163 g.

Example 5

A vinylsilicate-modified silica gel hydrophobed with dimethyldichlorosilane and heat stabilized by the addition of $FeCl_3$ was prepared.

A vinyl containing sodium silicate was prepared by adding 238 g of vinyltriethoxysilane to a solution comprising 103 ml of 48.4 weight percent NaOH in 225 ml of deionized water. This mixture was heated and ethanol removed by distillation. 50 ml of deionized water were added to the mixture and distillation continued until the pot temperature reached 103°C. The yield of vinyl sodium silicate was 163 g.

A silica hydrosol was prepared comprising 300 ml of PQ N Clear Sodium Silicate (PQ Corporation), 123 ml of the vinyl sodium silicate and 977 ml of deionized water. The silica hydrosol was added to a solution comprising 300 ml of concentrated HCl (Fisher Certified) and 300 ml of deionized water. This mixture was transferred to a 5 L flask and refluxed for 3 hours forming a vinylsilicate-modified silica hydrogel and then cooled to room temperature.

To the vinylsilicate-modified silica hydrogel, with stirring, was added 77 ml of dimethyldichlorosilane and 4.2 g of $FeCl_3$. After stirring the flask content at 65°C. for 1 hour, the content was cooled and 1.7 L of toluene were added to the flask. After stirring the flask content briefly, stirring was stopped and the aqueous phase drained from the flask. 250 ml of isopropanol and 60 ml of deionized water were added to the flask and the content of the flask stirred for several minutes. Then, 690 ml of deionized water were added to the flask and after stirring briefly the aqueous phase was drained from the flask.

The flask was fitted with a Dean-Stark trap and the toluene phase refluxed to remove residual water. The toluene phase was poured into glass pans and the toluene evaporated leaving as product a hydrophobic vinylsilicate-modified silica gel. The hydrophobic vinylsilicate-modified silica gel was dried for 24 hours at 75°C. The yield of dried hydrophobic vinylsilicate-modified silica gel was 202 g.

Example 6

A methylsilicate-modified silica gel hydrophobed with hexamethyldisiloxane and bis{3-(triethoxysilyl)-propyl}tetrasulfide and heat stabilized by the addition of $FeCl_3$

was prepared. A silica hydrosol was prepared by adding 312 ml of PQ N Clear Sodium Silicate (PQ Corporation), 140 ml of sodium methyl silicate (DC 722), and 948 ml of deionized water to a rapidly stirring solution comprising 300 ml of concentrated HCl (Fisher Certified) and 300 ml of deionized water. The silica hydrosol was transferred to a 5 L flask and 500 ml of concentrated HCl (Fisher Certified) were added to the flask. The flask content was refluxed for 3 hours, forming a methylsilicate-modified silica hydrogel, and then cooled to room temperature.

To the methylsilicate-modified silica hydrogel, with stirring, was added 833 ml of isopropanol, 120 ml of hexamethyldisiloxane and 3.1 g of $FeCl_3$. After stirring the flask content for 1 hour, 1.7 L of toluene were added. After stirring the flask content briefly, stirring was stopped and the aqueous phase drained from the flask. 250 ml or isopropanol and 60 ml of deionized water were added to the flask and the content of the flask stirred for several minutes. Then 690 ml of deionized water were added to the flask and after stirring the flask content briefly the aqueous phase was drained from the flask.

The flask was fitted with a Dean-Stark trap and the toluene phase refluxed to remove residual water. 10.7 ml of bis{3-(triethoxysilyl)propyl}tetrasulfide and 5.3 ml of trimethylchlorosilane were added to the flask. The flask content was refluxed for 1 hour with water being removed in the Dean-Stark trap. The toluene phase was poured into glass pans and the toluene evaporated leaving as product a hydrophobic methylsilicate-modified silica gel. The hydrophobic methylsilicate-modified silica gel was dried 24 hours at 75°C. The yield of dried hydrophobic methylsilicate-modified silica gel was 195 g.

Example 7

The dried hydrophobic organosilicate-modified silica gels prepared in Examples 1 and 2 were compounded into a silicone rubber composition, the composition cured, and the physical properties determined. Each of the dried hydrophobic organosilicate-modified silica gels was compounded at 38 parts per hundred (pph) into a polydimethylsiloxane gum containing 0.15 mole percent vinyl radicals substituted on silicon atoms and having a plasticity of 55 to 65. Into this base composition was blended 0.7 pph of 2,5-bis(t-butylperoxy)-2,5-dimethylhexane, based on the polydimethylsiloxane gum. The catalyzed base composition was cured in appropriate configurations for physical property testing by hot pressing at 34.5 MPa for 15 minutes at 175°C. The following test methods were used to test the cured silicone rubber: Tensile, ASTM D412; Elongation,

ASTM D412; 100% Modulus, ASTM D412; 50% Modulus, ASTM D412; Durometer (Shore A), ASTM 2240; Tear (Die B), ASTM D624; Tear (Die C), ASTM D624; Compression set (22h at 177°C), ASTM D395. Plasticities of the uncured compositions were measured on samples weighing two times the specific gravity of the composition that were formed into balls and rested one hour before measurement by ASTM D926. The results of this testing are provided in Table 1.

Table 1

Physical Properties of Silicone Rubber Reinforced With Hydrophobic Silica Gels

	EXAMPLE NUMBER		
	1		2
Property	No PC	P PC*	No PC
Plasticity	125	-	160
Tensile (MPa)	9.08	9.60	2.48
Elongation (%)	788	626	474
Modulus @50% (MPa)	0.63	0.88	1.12
Modulus @100% (MPa)	0.82	1.29	1.16
Durometer (Shore A)	48	56	62
Tear B (kN/m)	14.1	15.96	9.88
Tear C (kN/m)	12.7	16.5	21.58
Comp. Set. (% @ 22 h)	40.3	26.1	88.5

*Post cured for 4 hours at 250°C.

Claims:

1. A method for preparing a hydrophobic organosilicate-modified silica gel comprising:

(A) heating an organosilicate-modified silica hydrosol comprising (i) 2 to 50 weight percent of SiO_2 per milliliter and (ii) 1 to 50 weight percent of an organosilicate described by formula $R^1SiO_{3/2}$, where R^1 is a monovalent hydrocarbon radical comprising 1 to 6 carbon atoms, in the presence of a strong mineral acid at a pH less than pH 1 and a temperature within a range of 20 to 250°C. to form an organosilicate-modified silica hydrogel, and

(B) contacting the organosilicate-modified silica hydrogel with (1) a catalytic amount of a strong acid and (2) an organosilicon compound selected from organosilanes described by formula $R^2_aH_bSiX_{4-a-b}$ and organosiloxanes described by formula $R^2_nSiO_{(4-n)/2}$ where each R^2 is independently selected from hydrocarbon radicals comprising 1 to 12 carbon atoms and organofunctional hydrocarbon radicals comprising 1 to 12 carbon atoms, each X is independently selected from halogen and alkoxy radicals comprising 1 to 12 carbon atoms, a=0, 1, 2, or 3, b=0 or 1, a+b=1, 2, or 3 with the proviso that when b=1 then a+b=2 or 3, n is an integer of from 2 to 3 inclusive to form a hydrophobic organosilicate-modified silica hydrogel having a surface area within a range of 100 m^2/g to 750 m^2/g as measured in the dry state.

2. A method according to claim 1 where the organosilicate-modified silica hydrosol is heated at essentially pH 0.

3. A method according to claim 1 further comprising shearing the organosilicate-modified silica hydrogel of step (A) prior to conduct of step (B).

4. A method according to claim 1 where the contacting of step (B) is effected at a temperature within a range of about 20 to 250°C.

5. A method according to claim 1 further comprising contacting the hydrophobic organosilicate-modified silica hydrogel with a water-immiscible organic solvent in sufficient amount to convert the hydrophobic organosilicate-modified silica hydrogel to a hydrophobic organosilicate-modified silica organogel.

6. A method according to claim 1 further comprising during the contacting of step (B) the presence of a surfactant which facilitates reaction of the organosilicon compound with the organosilicate-modified silica hydrogel.

7. A method according to claim 1 further comprising during the contacting of step (B) the presence of a water-miscible solvent which facilitates reaction of the organosilicon compound with the organosilicate-modified silica hydrogel.

8. A method according to claim 1 further comprising mixing the organosilicate-modified silica hydrogel with an effective amount of a heat stabilizing agent selected from water soluble compounds of cerium and iron.

9. A composition prepared by the methods of claims 1, 3, 5 and 8.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 98/03123

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C01B33/16 C09C1/30

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C01B C09C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 3 122 520 A (CHARLES W. LENTZ) 25 February 1964 cited in the application see the whole document	1,2,4,5,7,9
Y	US 3 015 645 A (LESLIE J. TYLER) 2 January 1962 cited in the application see claims 1-12 see examples 6-9 see column 1, line 48 - column 3, line 41	1,2,4,5,7,9
A	GB 783 868 A (MIDLAND SILICONES LIMITED) 2 October 1957 see the whole document	1,4,5,7,9

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
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INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 98/03123

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
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A	DATABASE WPI Section Ch, Derwent Publications Ltd., London, GB; Class A26, AN 74-02910V XP002065965 & SU 369 131 A (SHAPATIN AS GOLDOVSKII EA) see abstract	1,8
A	FR 2 085 772 A (BAYER AG) 31 December 1971 see the whole document	1,8

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